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APPLICATION FOR LETTERS PATENT

OF

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FOR

HIGH SURFACE ZEOLITES AND METHODS FOR PREPARATION AND USE THEREOF

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High Surface Area Zeolites and Methods for Preparation and Use Thereof

Background of the Invention

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The present invention relates to high surface area faujasite zeolites, and methods for their preparation and use.

Faujasite materials are a well-known zeolite form and have a wide range of documented uses as catalyst supports, adsorbents, selective separation materials, etc. in the petrochemical and chemical industries and also as pollution control materials for industrial, domestic and automotive use. Faujasite materials, for example, are one of the main zeolitic materials proposed for hydrocracking use. Early findings showed that modification of the basic materials described in US-A-3,130,007 to produce a lowering of the unit cell size, gave improved selectivity to the desired middle distillate, or mid-barrel, products. To achieve this a combination of steam calcination and dealumination, usually acid-dealumination, techniques has been proposed, for example in GB-A-2,114,594; EP-A-98040; EP-A-247,679; and EP-A-421,422.

High silica to alumina molar ratio faujasites are also prepared by a combination of hydrothermal and (acid) dealumination techniques, such as those documented in US-6,054,113 and US-4,840,930, for example.

US-4,840,130 requires, for example, a specific temperature control program for the hydrothermal treatment in an attempt to minimize crystal destruction of the steamed faujasites in the subsequent acid dealumination required to raise the silica to alumina ratio of the zeolite.

US-6,054,113 in contrast requires the use, as starting materials, of "assynthesized" faujasite having a silicon to aluminum ratio of greater than about 4 to ensure that there is minimal crystallinity loss when subjected to subsequent cation exchange, a single steam calcination and a single acid dealumination. From the Examples, it is clear

that the single but lengthy steam calcination applied in this process causes a significant unit cell size reduction from greater than 24.40 Å for the unsteamed zeolite to less than 24.30 Å after steaming; since the desired unit cell size change is effected solely in the hydrothermal treatment step, this minimizes the need for extensive dealumination and also reduces the likelihood of crystal destruction in the acid-treatment step.

Summary of the Invention

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The inventors have now found that by careful selection of the starting materials, in particular by use of low alkali metal containing faujasite zeolites, and a carefully selected combination of moderate steam calcination conditions plus moderate acid or acid-ammonium dealumination conditions, it has been possible to obtain faujasite zeolites of low unit cell size, high surface area and an exceptional range of silica to alumina molar ratios (up to 1000), whilst still being able to retain a very high crystallinity.

Good activity can be expected from the zeolites of the invention in a number of important uses. In particular, a high adsorption capability for water and for hydrocarbon materials has been found. This has significance for pollution control uses, for example use in automotive catalytic converters.

The present invention provides a zeolite of the faujasite structure having a silica to alumina molar ratio (bulk) of greater than about 13, preferably 20 to 1000, more preferably 50 to 1000, especially 100 to 1000; a unit cell size in the range of from 24.10 to 24.40 Å; and a surface area of at least about 875 m²/g, preferably at least 950 m²/g, as measured by the BET method and ASTM D4365-95 with nitrogen adsorption at p/po values of 0.02, 0.03 and 0.04.

It has been found that by utilizing a combination of moderate steam calcination treatment and acid-dealumination treatment, it is possible to prepare faujasite-type zeolites which have these very desirable properties in the form of high surface area, low

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unit cell size and a useful micropore volume, without loss of crystallinity. Care has to be taken in the combination of treatment conditions utilized, on the one hand to avoid severe conditions in order to avoid destruction of the zeolite crystalline structure, but on the other not to utilize too moderate a set of conditions which, whilst producing a crystalline zeolite, will not produce the desirable high surface area of the zeolites of the present invention.

The present invention therefore provides a process for the preparation of a high surface area zeolite of the faujasite structure having a surface area of greater than about 875 m²/g which comprises:

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- a) providing a starting zeolite of the faujasite structure having a silica to alumina ratio of from about 4.5 to about 6.5 and an alkali level of less than about 1.5%wt;
- b) hydrothermally treating said starting zeolite at a temperature of 600 to 850 °C and at a partial pressure of steam of about 0.2 to about 1 atmosphere for a time effective to produce an intermediate zeolite having a unit cell size of from 24.30 to 24.45 Å;
- c) contacting the intermediate zeolite with an acidified solution comprising an acid and optionally an ammonium salt under conditions effective to produce a high surface area zeolite having a unit cell size of from 24.10 to 24.40 Å, a molar silica to alumina ratio of greater than about 13 and a surface area of greater than about 875 m²/g thereby producing the high surface area zeolite; and
- d) recovering the thus-contacted high surface area zeolite.

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the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

4. Claim 2 is rejected under 35 U.S.C. § 103(a) as being unpatentable over Knapp (US 4,704,017), as applied to claim 1 above, in further view of Onda et al. (US 5,244,470).

Knapp's teaching is detailed above. Although a specific example of pad printing is taught, the dots "may be deposited...in any manner" [c. 3, ll. 23-26].

Knapp does not explicitly teach that the dots are applied by screen printing.

Onda teaches a method in which a colorant is applied to the surface of a hydrophilic (soft) contact leans by screen printing [c. 3, l. 54 - c. 4, l. 11].

Since Knapp teaches that any method may be used to print the colored dots on the soft contact leans substrate, one of ordinary skill would have looked to the prior art for methods of applying colorant patterns to the surfaces of soft contact lenses. Since Onda teaches a method of doing so by screen printing, it would have been obvious to one of ordinary skill in the art to modify the method of Knapp so as to apply the colored dots by screen printing, as taught by Onda. One of ordinary skill in the art would have been motivated to do so by the desire end expectation of similar results: successfully coating the dots on the substrate.

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5. Claim 3 is rejected under 35 U.S.C. § 103(a) as being unpatentable over Knapp (US 4,704,017) as applied to claim 1 above, and further in view of Wingler et al. (US 4,533,397).

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hydrophilic material.

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Knapp's teaching is detailed above. As noted, the lens substrate may be made of

Knapp does not explicitly teach that the substrate is a polyester-polycarbonate alloy.

Wingler teaches a contact lens substrate manufactured from a polyester-polycarbonate alloy [abstract; c. 1, ll. 26-39; c. 2, l. 42 – c. 3, l. 2; c. 7, l. 51 – c. 10, l. 6].

Since Knapp teaches that the lens substrate may be made of hydrophilic material, but is not more specific, one of ordinary skill would have looked to the prior art for suitable hydrophilic lens substrates. Since Wingler teaches a hydrophilic lens of a polyester-polycarbonate material, it would have been obvious to one of ordinary skill in the art to modify the method of Knapp so as to utilize a polyester-polycarbonate alloy lens substrate, as taught by Wingler. One of ordinary skill in the art would have been motivated to do so by the desire and expectation of successfully providing a suitable lens substrate as well as a the expectation of forming a lens of increased comfort and resistance to infection [c. 1, 1, 57 – c. 2, 1, 2].

6. Claim 6 is rejected under 35 U.S.C. § 103(a) as being unpatentable over Knapp (US 4,704,017) as applied to claim 1 above, and further in view of Rawlings et al. (US 5,034,166).

Knapp's teaching is detailed above. As noted, the dots may be cured by heating.

Knapp does not explicitly state that the dots may be cured by UV light.

Rawlings teaches the application of colorant dots to a contact lens in which the colorant is UV cured [c. 6, l. 10-11 and c. 10, ll. 49-52].

particular very high SAR zeolites, can be prepared when just an acid, preferably a strong acid, is used in the dealumination step c).

The conditions which are useful to produce the high surface zeolitic materials of the present invention will of course vary depending on the type of acid and optional ammonium salt used, and on the conditions such as temperature and time under which the dealumination step is performed. Generally the temperature and time conditions for the dealumination step c) and the concentration of acid and optional ammonium solutions used, all work together to achieve the desired result, for example if the temperature is not at a sufficiently high level, then insufficient aluminum ions will be removed in the step c) to achieve the desirable zeolites.

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Step c) may be carried out at a temperature in the range of from ambient temperature, for example 20 °C, to 100 °C. Preferably an elevated temperature is used, most suitably in the range of from 40 to 80 °C. In the laboratory environment often the lower temperatures in the range are used; however on a commercial scale, the treatment temperatures may often be in the range of from 60 to 80 °C. If however materials having an exceptionally high silica to alumina ratio are particularly desired, then performing an acid-only dealumination at a temperature in the range of from 50 to 100, especially 80 to 100, in particular 80 to 95, °C has been found to be useful. The dealumination time may be in the range of from 0.5 hours to 10 hours, and is most conveniently from 1 to 5 hours. Naturally the higher the concentration of acid and optional ammonium salt used, the shorter the treatment time. Again, however, the timescale can vary from laboratory scale (where a batch treatment is usual) to the commercial scale (where continuous treatment is normal); in the latter the dealumination time may vary dependent on the throughflow of material in the treatment vessel.

The concentration of acid solution used is not critical. Useful materials have been prepared using hydrochloric acid in a concentration of as little as 0.7 milliequivalents H⁺

per g of zeolite to as much as 40. Most useful materials have been prepared using an acid dosage in the range of from about 5 to about 40, preferably from 9 to 20, milliequivalents H^+ per g of zeolite.

Equally the concentration of ammonium salt, when used, is not critical. Useful materials may be prepared using a dosage of from about 5 to about 40 milliequivalents NH₄⁺ per g of zeolite and generally of, about 10 to 20 milliequivalents NH₄⁺ per g of zeolite. It is generally desired however to use sufficient ammonium salt so that used alone or in combination with acid, the final alkali content is below 0.1% and more preferably below 0.04%.

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It is possible to perform either a single step or a multi-step dealumination in order to preserve the crystallinity of the zeolite treated but also to ensure, where necessary, that a mild acid treatment is performed in each step. It is thus possible that a treatment with 20 milliequivalents H⁺ per g of zeolite can be performed in two steps using 10 milliequivalents in each. Most conveniently each step is carried out using the same dealuminant materials and under the same reaction conditions.

Acids that may be used in step c) are inorganic acids or organic acids, for example acetic, formic or oxalic acids. Preferred acids are inorganic or mineral acids, having a pKa below 0 – often termed 'strong acids' in the art. Non-limiting examples of inorganic acids that can be used in the process of the invention are selected from hydrochloric acid, nitric acid, and sulfuric acid. Preferably a monovalent acid such as hydrochloric and nitric acid is used. Usefully the acid is used in the form of an aqueous solution.

Generally any ammonium salt may be conveniently used; suitable examples are ammonium nitrate, ammonium chloride, and ammonium sulfate. Preferably the ammonium salt used is selected from ammonium nitrate and ammonium chloride.

As a result of the dealumination treatment the unit cell size decreases and the silica to alumina molar ratio increases from that of the intermediate zeolite.

Step b) is a steam calcination step. Such treatments are common in the art and may alternatively be called hydrothermal treatments. Both terms are used in this text. In the process of the present invention, it is useful for the steam calcinations to be carried out at a temperature in the range of from 600 to 800 °C, and preferably from 650 to 750 °C. The steaming is most usefully carried out for in the range of from 0.5 hours to 5 hours, preferably 1 to 3 hours.

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Zeolites can be self-steamed where the steam water is provided by that which is released from the zeolite at high temperatures. In the present invention, steam is required preferably in an amount of at least 10% by volume (balance air, nitrogen or other inert gas). Usefully the steam is externally applied and not derived from the starting zeolite. Most preferably more than 90 % volume steam is present and especially about 100 %vol.

Most suitably the steam calcination treatment is carried out in two steps in which the first treatment is carried out at a different temperature than the second treatment. The temperature difference from first to second step or from beginning to end of a treatment is usefully from 10 to 100 °C, especially 20 to 50 °C. Care must be taken to ensure that hot spots do not occur in the treatment vessel, as this will yield zeolites of uneven properties.

The nature of the steaming treatment determines the conditions under which the dealumination treatment is carried out. For example using a slightly more severe steaming treatment (e.g. at a higher temperature) will cause a higher acid requirement to be needed to yield the high surface area zeolites. The best combination of conditions for the equipment and materials used can be routinely experimentally determined.

Preferably the hydrothermal treatment produces an intermediate material having a unit cell size in the range of from 24.33 to 24.38 Å. However if this unit cell size is not achieved, the high surface area zeolites can still be prepared through conducting the

dealumination step under mild conditions, for example at a low temperature, low acid dose and for a short duration, or to utilize a two-step dealumination.

A very suitable combination of hydrothermal treatment and dealumination treatment is performing steam calcination at a temperature in the range of from 650 to 750 0 C for 1 to 2 hours followed by an acid dealumination at a temperature in the range of from 40 to 95 0 C for 2 to 4 hours at an acid dosage in the range of from 6 to 20 milliequivalents per gram, optionally using an ammonium salt dosage in the range of from 10 to 30 milliequivalents per gram.

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Utilizing the process of the invention it is possible to prepare faujasite materials which have a unit cell size below about 24.40 angstroms, a surface area in excess of about 875 m²/g, a bulk silica to alumina molar ratio above about 13 and a useful micropore volume. Such materials are desirable for a wide range of uses, such as in adsorbency, selective separation, and pollution control.

The zeolites of the present invention find particular use as adsorbents, showing versatility in the type of material that can be adsorbed. Adsorption capability even at low partial pressure of adsorbate has been found for both polar and non-polar materials. This makes the zeolites of the present invention very attractive for general adsorbency use and for use in pollution control. As polar materials, water and polar hydrocarbons may be mentioned; as non-polar materials, non-polar hydrocarbons, such as aromatic hydrocarbons, for example benzene and toluene, may be mentioned. Accordingly the present invention also provides for use of the high surface area zeolites herein, preferably those having a SAR of 100 or more, as adsorbents.

The present invention will now be illustrated by the following Examples.

Examples

In the Examples the following test methods have been used:

<u>Unit cell size</u>: Determined by X-ray diffraction using the method of ASTM D-3942-80.

Surface Area: Determined in accordance with the conventional BET (Brunauer-Emmett-Teller) method nitrogen adsorption technique as described in the literature at S. Brunauer, P. Emmett and E. Teller, J. Am. Chm. Soc., <u>60</u>, 309 (1938), and ASTM method D4365-

- 95. Samples are pretreated before measurement at 500 °C for 4 hours. In the
- determinations quoted below, the results are given as multi-point assessments from measurements taken at a range of nitrogen partial pressures of p/p₀ of 0.02, 0.03 and 0.04.
 - Silica to alumina molar ratio (SAR): Determined by chemical analysis (either using X-ray fluorescence or atomic adsorption). Values quoted are 'bulk' SAR (that is to say the overall SAR) and not specifically the SAR of the crystalline framework.
 - <u>Total pore volume:</u> Determined via the BET method.

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- Micropore volume: Assessed by the t-plot method, also known as the t-method, using nitrogen as the adsorbate as described by Lippens, Linsen and de Boer, Journal of Catalysis, 3,32 (1964).
- Crystallinity: Determined by modification to ASTM D3906-97: this utilizes X-ray diffraction, and is expressed as the percentage retained or increased crystallinity of the final zeolite relative to a standard zeolite Y. Since the materials of this invention are all of the low unit cell variety, we have chosen to report their relative crystallinity versus a material of like kind, i.e a standard with similar unit cell size. Therefore, conclusions reached are valid in relation to that standard or more importantly in and among the data presented herein. In any event the micropore volume should be used as a more definitive measure of the zeolite content of these type materials and these crystallinity data used only for corroboration.
 - Comments on the Method of Surface Area-Micro Pore Volume Analysis:
- Zeolite quality has in the literature generally been described using BET surface area. The surface area data presented here have been determined by the general procedure described

in ASTM method D4365-95. The specific recommendation in the ASTM method is that for high zeolite content materials the linear BET range is preferentially found between p/p_0 values of 0.01 and 0.09. The method further states that emphasis on the lower p/p_0 values should be used if a negative intercept is observed. In addition Johnson (Journal of Catalysis 52, 425-431 (1978), "Estimation of the Zeolite Content of a Catalyst from Nitrogen Adsorption Isotherms") clearly shows that very little adsorption of nitrogen occurs above a p/p_0 value of 0.05 with zeolite Y and zeolite Y catalysts. Therefore, we have selected the adsorption at nitrogen partial pressures of 0.02, 0.03 and 0.04 p/p_0 as the most suitable from which to calculate a BET surface area for the zeolites herein.

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The materials described in these Examples contrast in particular in surface area compared to generally available, commercially available dealuminated materials and those documented in the literature of the art. Care must be taken to compare them to materials with similar unit cell dimensions. (For example, WO 00/20332 discloses faujasite zeolitic materials with a surface area of at least 800 m²/g but at a unit cell size range of 24.40 to 24.65 Å.) Such materials have in the patent literature been referred to as "Ultrahydrophobic zeolite Y" (UPHY). GB-A-2,014,970 describes materials with unit cell parameters less than 24.45 angstroms as having BET surface areas from 450 m²/g to about 600 m²/g. US 4,401,556 describes the use of such UPHY materials (and catalysts based on them) having surface areas in the range of from 520 to 579 m²/g. EP-A-421 422 documents zeolites that have recorded BET surface areas of from 586 to 752 m²/g.

Commercially available materials are also referenced in the literature. In particular US 5,234,876 references "Ultra-stable Y-zeolite" materials, TSZ-350 and TSZ-360 available from Tosoh Corporation with BET surface areas ranging from 600 to 650 m²/g. Similarly, Bezman in Catalysis Today, 13, 143-156 (1992) describes hydrothermally dealuminated Y-type zeolites (HDY's) available from the Linde Division of UOP.

specifically LZ-Y20 and from PQ Corporation, specifically CBV 600 and CBV 712. All these materials are reported to have BET surface areas between 500 and 700 m²/g.

Preparation of zeolites

Zeolites of the present invention and comparative zeolites were prepared by the following general procedures.

In these Examples, the starting materials are low alkali content (<1.5 %wt alkali

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oxide) ammonium form Y zeolites. These zeolites are prepared by one of two methods known in the art. While not meaning to be exclusive of other methods of achieving similar results, the examples were prepared by either the Cooper method (as described in U.S. Patent Specification No. 5,435,987) which involves K⁺ ion exchange of Na form zeolite Y, followed by ammonium ion exchange, or by the Alafandi method (as described in U.S. Patent Specification No. 4,085,069) which involves ammonium exchange under autogenous superatmospheric pressure. The chemical analysis of the starting zeolites

along with the details of method of preparation is indicated in Table 1.

The low alkali content ammonium form Y zeolites were steam calcined in either one or two steps to create an ultrastable type Y zeolite. The steamed zeolites were then subjected to an acid-dealumination treatment consisting of either a one or two-step treatment with a combination of an ammonium salt and an inorganic acid. The specific details of the steaming treatment(s) and the acid-dealumination treatment are also given in Table 1. The water content in the acid-dealumination treatment was generally sufficient to provide a zeolite slurry with from 5 to 25%wt anhydrous zeolite. Such variation is not believed to materially affect the results obtained.

Product properties of the materials of Examples 1 to 14 are given in Table 2.

Table 1. Preparation Methods for Examples 1 to 14

Starting NH ₄ Y	Ex. 1	Ex. 2	Ex. 3	<u>Ex. 4</u>	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Ammonium Exchange	Alafandi	Cooper	Cooper	Cooper	Cooper	Cooper	Cooper	Cooper
Method				-	•	•	•	
K ₂ O, %wt	<0.04	0.65	0.65	0.62	0.82	1.10	0.65	0.21
Na ₂ O, %wt	0.25	< 0.04	< 0.04	<0.04	< 0.04	< 0.04	< 0.04	< 0.04
SiO ₂ /Al ₂ O ₃ , mole ratio <u>Preparation Details</u>	5.0	5.1	5.1	5.1	5.1	5.5	5.1	5.2
Calcination No. 1 Temperature, °C Time, hrs Steam content, %vol	650 3 94%	630 1 100%	630 1 100%	650 1 100%	650 1.5 100%	650 1 100%	630 1 100%	630 1 100%
Calcination No. 2 Temperature, °C Time, hrs Steam content, %vol	- - -	650 1 100%	650 1 100%	- - -	- - -	- - -	650 1 100%	650 1 100%
Unit cell constant of intermediate, Å Dealumination-Ion Exchange 1st Contact	24.37	24.38	-	-	•	24.39	24.38	24.33
Temperature, °C	40	40	40	40	40	40	40	40
Time, hrs	4 Cl	5	5	5	5	5	5	5
Anion system Milliequivalents H ⁺ per gram	9	Cl ⁻ 10	C1 ⁻ 9	Cl ⁻ 10	OI.	Ol.	CI ⁻ 10	Cl ⁻ 10
Milliequivalents NH ₄ ⁺ per	20	19	20	19	20	20	19	19
gram 2 nd Contact								
Temperature, °C	-	-	-	-	-	-	-	-
Time, hrs Anion system		-	-	-	-	-	-	-
Milliequivalents H ⁺ per gram	-	-	-	-	-	-		-
Milliequivalents NH ₄ ⁺ per	-	-	-	-	-	-	-	-
gram								

Table 1. Preparation Methods for Examples 1 to 14 (cont'd)

Starting NH ₄ Y	<u>Ex. 9</u>	Ex. 10	Ex. 11	Ex. 12	Ex. 13	<u>Ex. 14</u>
Ammonium Exchange Method	Alafandi	Alafandi	Cooper	Cooper	Cooper	Cooper
K ₂ O, %wt	<0.04	<0.04	0.66	0.66	0.53	< 0.04
Na ₂ O, %wt	0.25	0.25	<0.04	< 0.04	0.67	0.66
SiO ₂ /Al ₂ O ₃ , mole ratio	5.0	5.0	5.5	5.5	5.0	5.5
Preparation Details						
Calcination No. 1						
Temperature, °C	650	600	650	650	687	675
Time, hrs	3	1	2	2	3	2
Steam content, %vol	93%	100%	100%	100%	100%	100%
Calcination No. 2						
Temperature, °C	-	700	-	-	-	-
Time, hrs	-	1	•	•	-	•
Steam content, %vol	-	100%	-	-	-	-
Unit cell constant of intermediate, Å Dealumination-Ion Exchange 1st Contact	24.41	-	24.38	24.38	24.36	-
Temperature, °C	40	40	60	60	93	93
Time, hrs	5	5	3	3	3	3
Anion system	Cl	Cl	Cl	Cl	NO ₃	Cl
Milliequivalents H ⁺ per gram	11	9	6	7.5	0.7	1.1
Milliequivalents NH ₄ ⁺ per gram 2 nd Contact	20	20	37	37	12	37
Temperature, °C	_	_	_		93	60
Time, hrs		_	_	_	3	2
Anion system	-	_	-	•	NO³.	Cľ
Milliequivalents H ⁺ per gram	-	-	-	-	0.7	2.2
Milliequivalents NH ₄ ⁺ per gram	-	-	-	-	12	37